

ANALYSIS OF NONDISTILLABLES FROM COAL LIQUIDS BY SIZE EXCLUSION  
CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED SPECTROMETRY (SEC/FT-IR)

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INTRODUCTION

Coal liquids may contain as much as 50% or more nondistillables. Most of the nondistillable materials are soluble in solvents such as tetrahydrofuran (THF) or pyridine. Currently, the nondistillables are characterized by elemental analysis, nuclear magnetic resonance (NMR), Fourier Transform infrared (FT-IR) spectrometry and heating values. The nondistillable and distillable fractions of a coal liquid can be separated and analyzed by size exclusion chromatography (SEC) (1-8). SEC separates molecules based on "linear molecular" size (3,4). The application of SEC is limited only by the solubility of the sample in a solvent. Although SEC has been used primarily for the separation and characterization of polymers based on molecular size or molecular weight, its use has been extended to the separation of smaller size molecules (10-13).

The separation of coal liquids by SEC is easily achieved with appropriate columns. Because coal-derived mixtures have several components of a similar size, the use of SEC alone is not adequate for the purpose of identification. Gas chromatography (GC) coupled with mass spectrometry (MS) has been used in conjunction with the SEC (14,15,16). The use of these three analytical techniques [SEC, GC, and MS] is a powerful analytical method for the analysis of the distillables of coal liquids, recycle solvents and anthracene oils (14, 15, 16).

Analysis of SEC fractions of nondistillables by FT-IR spectrometry is very useful in characterizing the coal liquids produced under different reaction conditions. Conventional FT-IR techniques are rather unreliable as well as time consuming, because the mass of coal liquid in a SEC fraction is very small. A new technique, which is more reliable and requires less time than the conventional techniques, is developed for the analysis of small samples. The residues from SEC fractions are spotted onto a potassium bromide (KBr) pellet. The spotted samples are then analyzed using a narrow focused beam in the Microbeam accessory of a Nicolet 60 SXR FT-IR spectrometer. The paper discusses the analytical technique as well as the FT-IR spectra of SEC fractions.

EXPERIMENTAL

The low rank coal used in the liquefaction experiments (15) was Zap-2 Indian Head lignite from North Dakota. Mini-reactors (6.3 and 20 ml), which were made from Autoclave high pressure fittings (7) were used. The liquefaction solvents included anthracene oil and water under supercritical conditions. Hydrogen, carbon monoxide and hydrogen sulfide were the reactive gases. The experimental conditions are listed in Table 1, and the yields are listed in Table 2 (15).

Coal liquids from these experiments were separated by distillation at 230°C and 1 Torr. The nondistillables were dissolved in THF and separated using a 60 cm long, 5  $\mu$ m, 10 nm PL gel column and THF as the mobile phase. The effluents were monitored by a Waters refractive index detector (Model 401). The SEC fractions were collected as one ml fractions. Most samples were separated into

10 fractions. The THF in these fractions was evaporated using a slow dry stream of nitrogen and occasionally warming the vials with warm air from a hot air blower. The residues were used for FT-IR analysis.

A Nicolet 60SXR FT-IR Spectrometer with Microbeam accessory and a MCT-A detector was used for the FT-IR analysis. The samples were dissolved in 2-5 ml and spotted on a 13 mm potassium bromide (KBr) pellet (100 mg) using a 5 ml syringe with a fused silica needle. The pellets were dried on a hot plate. Six 1-2 mm diameter sample spots were deposited on each KBr pellet. Each pellet was scanned using a motorized sample stage which is both manual and computer software controllable. The Microbeam accessory is used to focus the IR beam either manually or by the 60 SXR software. A narrow beam (0.1 mm dia.) was used for the analysis. The Microbeam accessory enables analysis of a sample as small as 0.1 mg with good absorption spectrum with about 2 absorbance unit for the largest peak. Absorptions due to water vapor and CO<sub>2</sub> were subtracted from all spectra. The spectra were subjected to baseline correction as well as the normalization of the largest peak to 2.00 absorbance units.

## RESULTS AND DISCUSSIONS

The coal liquids contained substantial amounts of nondistillables, which varied depending on the reaction conditions. Figure 1 shows the distribution of various chemical species in a coal liquid. A coal liquid from Wyodak subbituminous coal is used for the illustration.

One of the major results of SEC-GC-MS analysis of the distillables is the discovery of an orderly pattern (14,15,16), by which various isomers and homologues of similar chemical species exist in coal liquids. Direct coal liquefaction produces chemical species, which differ from each other by size and extent of isomerization but with an orderly continuous pattern. Alkanes ranging from C<sub>12</sub>H<sub>26</sub> and C<sub>44</sub>H<sub>80</sub> are detected in almost any coal liquid. Most of these are straight chain alkanes showing an orderly continuous pattern. Neither is a particular n-alkane almost absent nor is it present in a disproportionate amount. Exceptions exist for some branched alkanes such as pristane, phytane, and hopanes. These species are also called biomarkers and their concentration varies depending on the sample. The nondistillable fraction of coal liquids are expected to contain larger alkanes as a continuation of the alkane pattern. Since alkanes larger than nC<sub>44</sub>H<sub>80</sub> are almost insoluble in THF, their presence in THF soluble nondistillables is limited and they may exist as nondistillables in the THF insoluble fractions.

Phenols are a major group of species present in coal liquids and have basically one or more aromatic ring structures with alkyl substituents. Methyl, ethyl and propyl are the most common alkyl substituents (14,15,16). The number of possible isomers increases as the possible number and size of alkyl substituents increases. It is expected that higher degrees of alkylation can produce larger molecules with a greater number of isomeric forms. Separation of these isomers is rather difficult even by high resolution GC methods. The larger phenols should be present in the nondistillables. If pattern observed for the distillables is continuous, the phenols are heavily alkylated and may contain other functional groups including additional hydroxy groups. SEC can separate these phenols based on "linear size" (length obtained from valence bond structures), and FT-IR gives an insight into the structural details. Interpretation of the FT-IR is difficult (17-20) and requires extensive use of the literature as well as conformation from other analytical methods.

The number of isomers of alkylated aromatics is enormous. Increased alkylation causes an increase in the number of isomers. In the case of both alkylated phenols and aromatics various isomers exist in a continuous pattern

(14,15,16). A low amount of alkylation gives a few well-resolved isomers. For aromatic species which have been extensively alkylated a large number of isomers are produced but in small concentrations. The two types of aromatics are expected in the nondistillables. Polycyclic aromatics such as pyrenes and coronenes are the first type which appear in SEC fraction 10. The second type is the alkylated aromatics which are heavy due to size and number of alkyl side chains. The trend in distillables indicates that the number of possible isomers is enormous. The use of FT-IR with SEC allows one to identify the functional groups for molecules with a known linear molecular size.

The THF soluble nonvolatiles shown in Figure 1 represent the nondistillables in a coal liquid. If we assume that the heavy alkanes are insignificant due to their limited THF solubilities, the nonvolatiles contain two major chemical species, i.e. alkylated phenolics and aromatics. Phenolic species will be found in the first few SEC fractions and the aromatics in the last few fractions.

Figures 2-4 illustrate the separation of three coal liquids by SEC. By using the Microbeam accessory on the FT-IR and the new technique, the small samples in the SEC fractions are readily analyzed. The Microbeam accessory is used to focus the IR beam to less than 0.5 mm diameter, and analyze small samples deposited as spots on a KBr pellet. This technique allows the analysis of up to six sample spots on a single 13 mm diameter pellet. Another advantage of this technique is that the area between the spots on the pellet is used for background subtraction to eliminate the absorptions from contaminants in the pellet such as absorbed water.

FT-IR has been used to characterize spectroscopic analysis of complex substances such as coal, oil shale, petroleum crude and various products derived from them (18-20). These fossil fuels as well as coal liquids are composed of various species with functional groups whose characteristic absorption bands may overlap and interfere with the interpretation of the spectra. We have shown (3,4) that SEC separates molecules on the basis of linear molecular size, and that the phenolics hydrogen bond with the THF. Thus SEC with THF solvent is capable of separating phenolics and aromatics. Therefore, SEC separation prior to FT-IR analysis is used to resolve some of the uncertainties associated with spectral interpretation.

Figure 5 shows the FT-IR spectra of 10 one ml SEC fractions of nondistillables from a liquefaction reaction in where water under supercritical conditions was used as the solvent along with reactive gases such as  $H_2$ , CO and  $H_2S$  (See Table 1 & 2 for experimental conditions and product yields). Most reports on FT-IR analysis of coal points out the difficulties associated with the interpretation of the spectrum. A good discussion about the band assignments of functional groups found in coal and coal liquids is presented in a recent paper (19). Figure 6 shows the SEC/FT-IR analysis of anthracene oil distillate which was also used as solvent for liquefaction experiments. The effect of reaction time on the SEC/FT-IR data for the nondistillables produced when using anthracene oil distillate and water under supercritical conditions is illustrated in Figure 7.

Comparison of Figures 1,2,3 & 4 shows that any coal liquid sample can be separated over a 10 ml THF flow time. The first five fractions contain most of the nondistillables and the latter five fractions have most of the distillables.

The broad absorbing peak at  $3400\text{ cm}^{-1}$  in all spectra shown in Figures 5-7 indicate the species with phenolic or alcoholic hydroxy groups. The nondistillables from all four liquefaction experiments have species with hydroxyl group in the first six SEC fractions. SEC fractions 7 through 10

showed smaller amounts of phenols in two experiments (TEH 11 & 22) and very little in the other two experiments (TEH 13 & 23). The product from the two short reaction time experiments (TEH - 13 and 22) have a larger broad peak at  $3400\text{ cm}^{-1}$  indicating more large molecular size phenols than the product produced in the two longer reaction time experiments (TEH 11 and 23). The absorption due to the phenolics reaches a maximum for SEC fraction 6 for two runs (TEH 22 & 23) where supercritical water was the solvent, and at SEC fraction 4 for one run (TEH-11) where anthracene oil and long reaction time were used. Short reaction time experiment (TEH-13) with anthracene oil followed an intermediate trend. The absorption at  $2900\text{ cm}^{-1}$  due to alkyl groups maximized in SEC fraction 5 for all coal liquid samples.

The broad absorption peak at  $1700\text{ cm}^{-1}$  is due mostly to various carbonyl groups. Short reaction time experiments (TEH-13 & 22) showed an increase in the amount of carbonyl groups in SEC fractions 2-5 as indicated by the single broad peak at  $1700\text{ cm}^{-1}$ . Longer reaction time experiments (TEH 11 & 23) show smaller absorptions in SEC fractions 2-5 with a split broad peak. Longer reaction time experiment (TEH-11) showed an increase in the amount of carbonyl absorption in SEC fraction 6-10, compared to the shorter reaction time experiment (TEH -13). The absorption at  $1600\text{ cm}^{-1}$  appears to be due to aromatic species with substituents such as alkyl, carbonyl and hydroxy groups. These species did not show any trend in any of the SEC fractions, or with reaction conditions.

#### CONCLUSION

The use of Microbeam accessory and the spotting of the sample on the KBr pellet enables the study of small samples of coal liquids by FT-IR combined with SEC. The analysis time is short and reproducible. The complex and unknown chemical composition of nondistillables in coal liquids makes the determination of the chemical significance of each IR absorption peak rather difficult. This is particularly the case with the limited number of experiments used in this report. But it appears that the nondistillables and distillables contain species with similar functional groups. The determination of the structure of nondistillables may be possible by use of the FT-IR data, and by extrapolation, using the known chemical nature of major species in distillables.

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Table 1. Liquefaction conditions

Run No.	Temp. (K)	H <sub>2</sub> (%)	CO (%)	H <sub>2</sub> S (%)	Time (min.)	Max P (MPa)	Solvent
TEH-11	681	38.4	44.1	17.5	22.8	29.2	A04
TEH-13	690	38.4	44.1	17.5	4.4	23.2	A04
TEH-22	695	33.2	41.8	25.0	4.5	34.6	H <sub>2</sub> O
TEH-23	695	33.2	41.8	25.0	19.8	34.6	H <sub>2</sub> O

Table 2. The Percentage yields based on dmmf lignite.

Run No.	NDTHFS	Distillables
TEH-11	30.40	49.93
TEH-13	50.76	6.79
TEH-22	33.04	16.38
TEH-23	47.22	18.58

THF = Tetrahydrofuran, NDTHFS = THF soluble nondistillables.

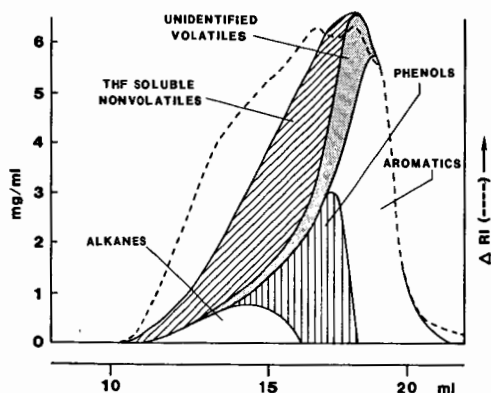


Fig. 1 SEC separation of Wyodak recycle solvent. The reconstructed chromatogram is shown to illustrate the size distribution various chemical species.

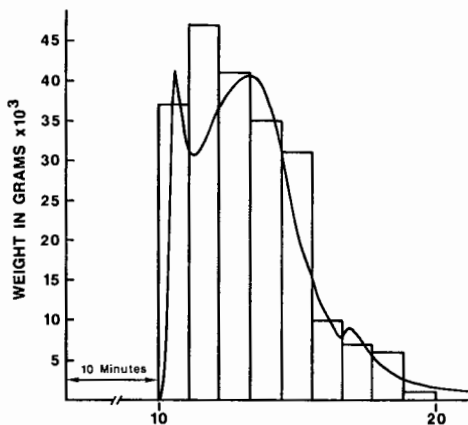


Fig. 3 SEC separation of THF soluble nondistillable from liquefaction experiment TEH-11. The solid curve shows the  $\Delta$ RI responded.

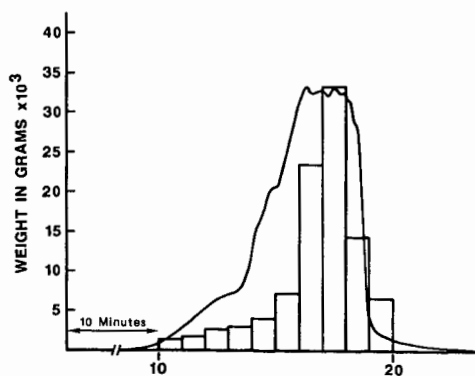


Fig. 2 SEC separation of Anthrazene oil which was used in liquefaction experiment TEH-11. The solid curve shows the  $\Delta$ RI responded.

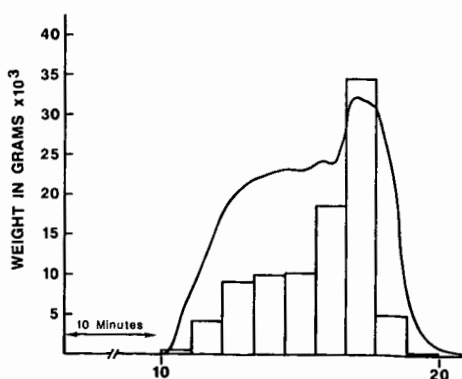


Fig. 4 SEC separation of THF soluble products from liquefaction experiment TEH-11. The solid curve shows the  $\Delta$ RI responded.

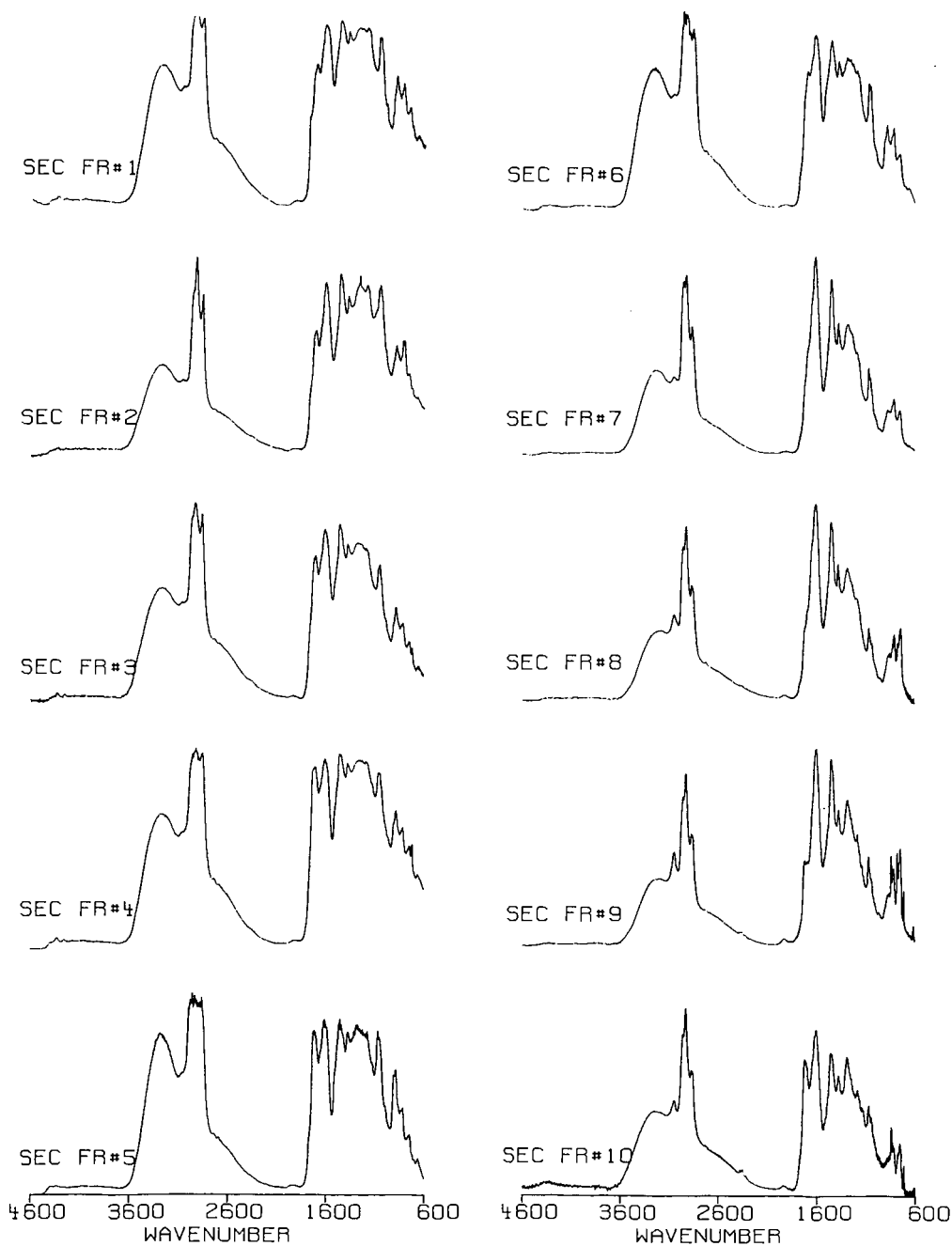


Fig 5. FT-IR spectra of SEC frs. of nonvolatiles from Zap-2 lignite liquefield using water under supercritical condition. See Table 1 & 2 for the reaction conditions & yield of TEH 22.

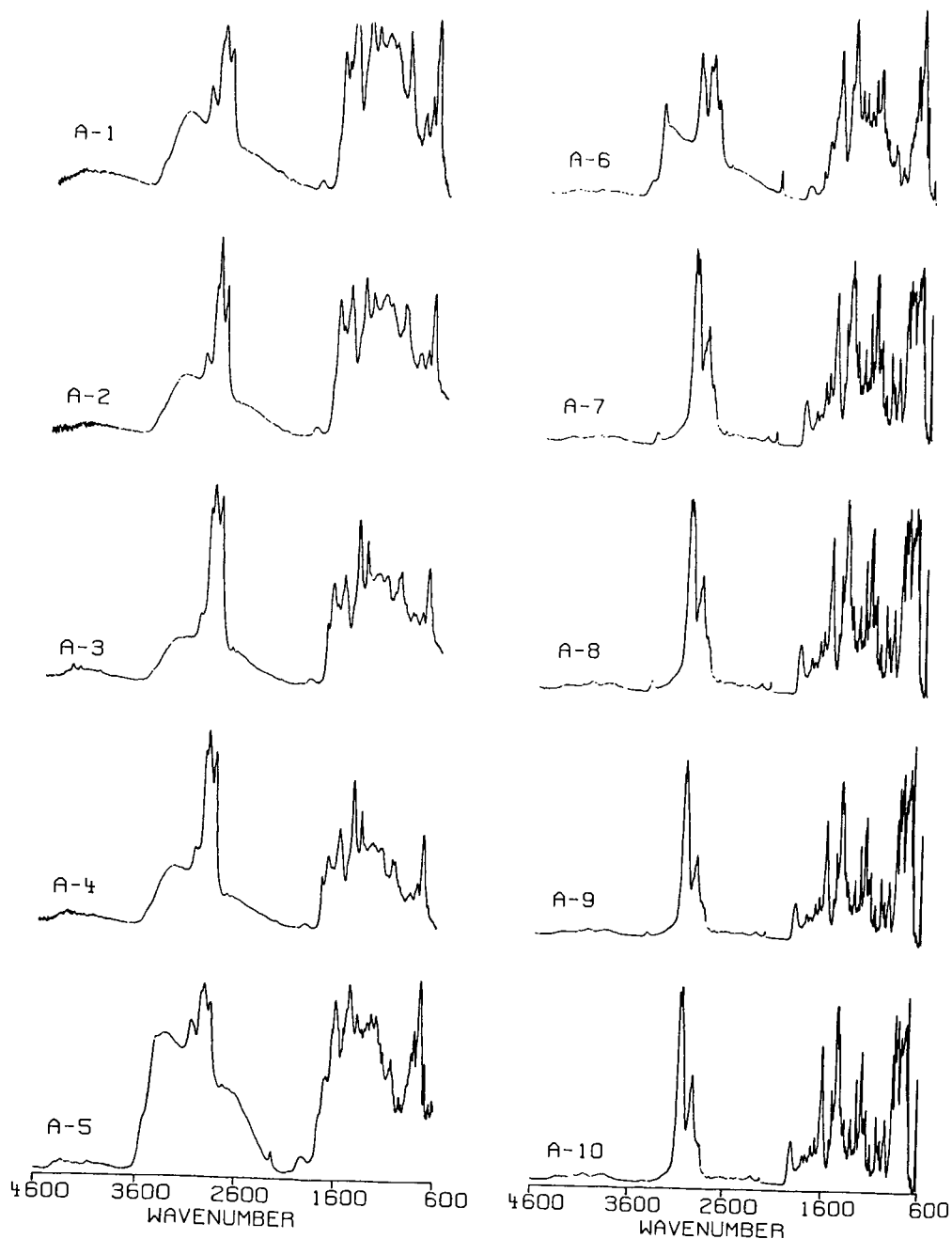


Fig 6. FT-IR spectra of SEC fractions of Figure 2 Anthracene oil distillate (A04). Figure 2 shows the SEC of A04.



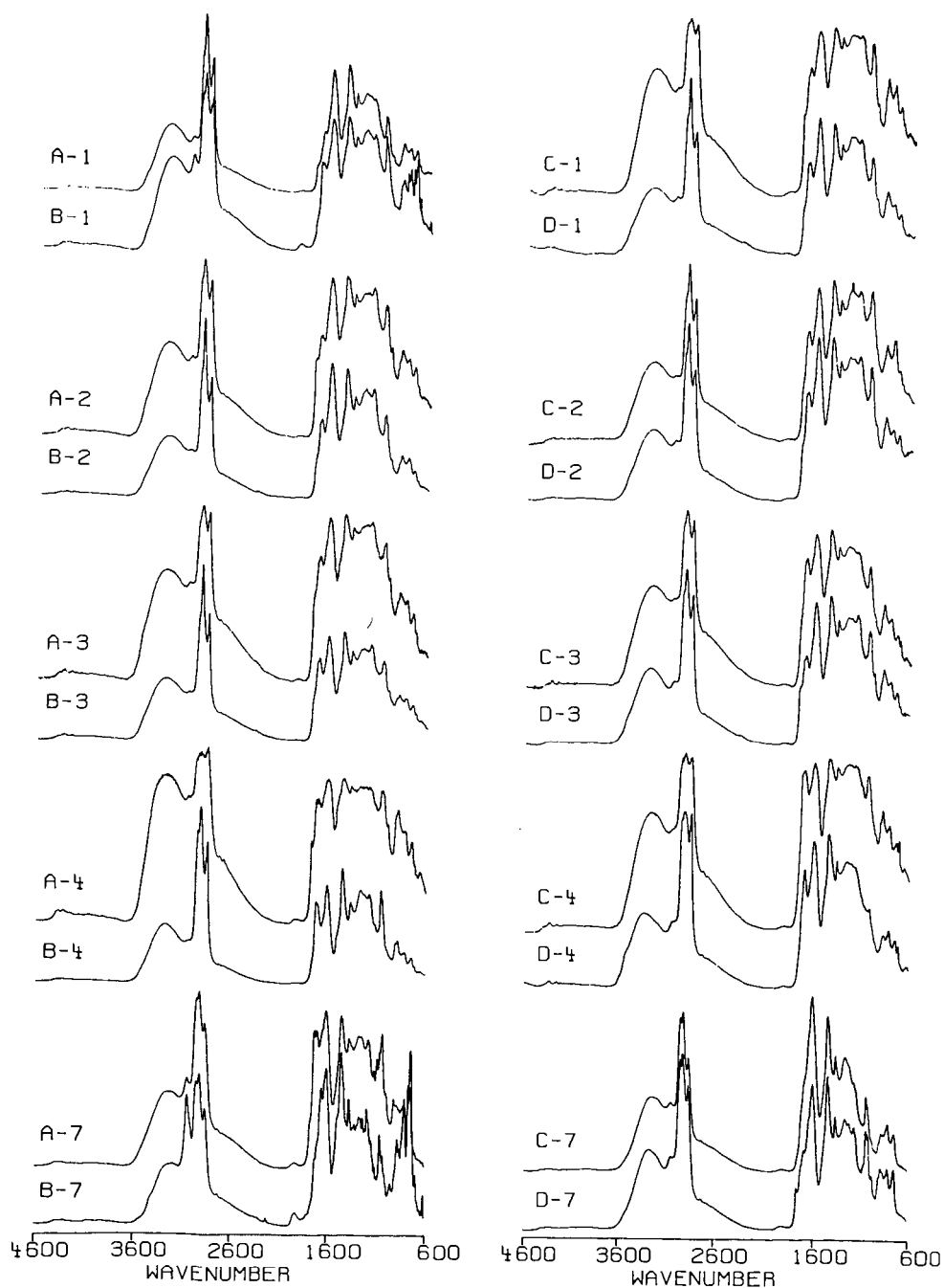


Fig 7. Comparison of FT-IR spectra of SEC fractions of non distillate obtained from four liquefaction experiments - A = TEH 13 and B= TEH 11 c= TEH 22 and D=TEH 23.